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㉞ Patentinhaber:
Minnesota Mining and Mfg. Co., Saint Paul, Minn.,
US

㉝ Vertreter:
Vossius & Partner, 81675 München

㉞ Benannte Vertragstaaten:
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㉒ Erfinder:
Chou, Hsin-Hsin 3M Company, Saint Paul,
Minnesota 55133-3427, US

㊼ Laserinduziertes Aufzeichnungsverfahren mit thermischer Übertragung durch Wärme

(54) **Laser-induced thermal transfer imaging process**

Laserinduziertes Aufzeichnungsverfahren mit thermischer Übertragung durch Wärme

Procédé pour l'enregistrement par transfert thermique induit par laser

(72) Inventor:
Chou, Hsin-Hsin
3M Company
Saint Paul, Minnesota 55133-3427 (US)

(74) Representative:
VOSSIUS & PARTNER
Postfach 86 07 67
81634 München (DE)

(56) References cited:
US-A- 5 171 650   US-A- 5 326 619

Description

Field of the Invention

5   **[0001]** This invention relates to laser addressable imaging films, in particular, to photo-induced thermal transfer or ablation imaging films having reduced interference patterns in the final image.

Discussion of the Art

10   **[0002]** With the increase in electronic imaging information capacity and use, a need for imaging systems capable of being addressed by a variety of electronic sources is also increasing. Examples of such imaging systems include thermal transfer (dye and mass transfer), ablation (or transparentization) and ablation-transfer imaging. These imaging systems have been shown to be useful in a wide variety of applications, such as, color proofing, color filter arrays, printing plates, and reproduction masks.

15   **[0003]** The traditional method of recording electronic information onto a thermal transfer imaging medium utilizes a thermal printhead as the energy source. The information is transmitted to the printhead causing a localized heating of a thermal transfer donor sheet which then transfers material corresponding to the image data to a receptor sheet. The two primary types of thermal transfer donor sheets are dye sublimation (or dye diffusion transfer) and thermal melt transfer. Representative examples of these types of imaging systems can be found in US Patent Nos. 4,839,224 and

20   4,822,643. The use of thermal printheads as an energy source suffer several disadvantages, such as, size limitations, slow image recording speeds, limited resolution, limited addressability and artifacts on the image due to detrimental contact of the media with the printhead.

   [0004] The increasing availability and use of higher output compact lasers, semi-conductor light sources, and particularly laser diodes which emit in the visible and particularly in the near-infrared and infrared region of the electromag-

25   netic spectrum, have allowed the use of these sources as viable alternatives for the thermal printhead as an energy source. The use of lasers and laser diodes as the imaging source is one of the primary and preferred means for transferring electronic information onto an image recording media. Lasers and laser diodes provide higher resolution and more flexibility in format size of the final image than the traditional thermal printhead energy sources. In addition, the use of lasers eliminates detrimental effects from contact of the media with the heat source. As a consequence, a need

30   exists for media that have the ability to be efficiently exposed by these sources and which have the ability to form sharp images of high resolution and sharpness.

   [0005] It is well known in the art to incorporate light-absorbing layers in the thermal transfer constructions to act as light-to-heat converters. This then allows one to use lasers or laser diodes as energy sources. Gas-producing materials may also be incorporated into constructions known as propellant-containing thermal transfer or ablation-transfer ele-

35   ments which are also compatible with laser or laser diode sources. Representative examples of these laser or laser diode imageable elements can be found in U.S. Patent Nos. 5,308,737; 5,278,023; 5,256,506; and 5,156,938.

   [0006] When thermal imaging elements are exposed with coherent radiation (e.g., lasers or laser diodes) at a uniform exposure level across the entire surface of the element, a very distinct interference pattern resembling the grain pattern in wood is produced. These patterns tend to be neither symmetrical nor repetitive, and like the grain pattern in polished

40   woods, appear as variations in optical density (lightness and darkness) in the imaged element. Such visible patterns are highly undesirable in any imaging system, especially where the quality of the image is critical.

   [0007] In laser electrophotography, interference patterns in the image have been attributed to variations in the reflectivity of the layers within the electrophotographic organic photoconductor (OPC). See, for example, Imaino, W.I., et al, *SPIE Proceedings Lasers in the Graphic Arts - Congresses,* High Speed Read/write Techniques for Advanced Printing

45   and Data Handling, Vol. 390 (1983); and Williams, E.M., The Physics and Technology of Xerographic Processes, John Wiley & Sons, New York, p 96-98 (1984). Light scattering or diffusion techniques have been used to remove the phase relationship of the incident and the reflected light beams, such as, incorporation of particulates in surface coatings, interlayers and backside coatings.

   [0008] U.S. Patent No. 4,617,245 discloses the use of a coated photoconductor wherein the thickness of the coating

50   layer is regularly changed within the minute width of the coating layer by providing an electroconductive substrate having linear projections and tapered reflective surfaces to eliminate interference fringes in the formed image.

   [0009] U.S. Patent No. 4,711,838 discusses the problem of non-contact interference scanner fringes associated with laser imaging of near-infrared (NIR) sensitized photographic films. The formation of interference fringes is eliminated by the use of a combination of diffuse transmitting, reflecting, or absorbing layers.

55   **[0010]** The use of anti-reflection coatings to reduce the reflection of optical surfaces has been studied extensively. For example, the use of inhomogeneous anti-reflection coatings and, in particular, multilayer anti-reflection coatings are known to improve performance of a film or substrate. (Musset, A, and A. Thelen, "Multilayer Antireflection Coatings", Progress in Optics, VIII, p 202-207 (1970).)

[0011] In U.S. Patent No. 4,8▮▮,▮33, a silica coating comprising colloidal silica particles i▮ ▮cribed which increases the transmission of a transparent substrate by at least 2 percent and reduces the specular reflectance. The voids of the porous silica costing provide a multiplicity of subwavelength interstices where the index of refraction abruptly changes from that of air to that of the coating material.

[0012] Photographic diffusion transfer films using anti-reflection coatings containing fluorinated polymers are described in U.S. Patent Nos. 3,793,022 (fluorinated polymers with an index of refraction at least 0.2 less than the transparent support) and 4,769,306 (fluorinated polymers dispersed in a silica matrix). Anti-reflection coatings containing fluorinated polymers are also disclosed in U.S. Patent Nos. 5,256,506; 5,171,650; and 5,156,938 for use in ablative transfer elements. The use of the anti-reflection layer in these systems is believed to enhance the efficiency of the imaging process by enabling more of the imaging radiation to be effectively utilized.

[0013] In U.S. Patent No. 5,326,619 and U.S. Patent No. 5,459,016 laser-addressable thermal transfer donor elements are described where a black aluminum layer is deposited upon a microstructured surface. The black aluminum layer conforms to the microstructured surface thus providing increased surface area which enhances the conversion of radiant energy to heat and the diffusion of that heat from the black metal to the surrounding gas-producing polymer and/or thermal mass transfer material in the adjacent layer.

[0014] Many of the approaches described above to address internal reflections are not suitable in a thermal transfer system. For example, materials which absorb the radiation from the imaging source significantly reduce the efficiency of the system. Materials that use scattering effects to reduce reflection, such as large silica particles, lower the resolution of the image. To optimize the effect of conventional antireflection coatings, the coating thickness must be carefully controlled using precision coating methods. Thus, there is a need for materials which reduce interference patterns in laser addressed thermal transfer imaging systems without interfering with the advantages of the high speed and resolution afforded by the use of lasers or laser diodes.

Summary of the Invention

[0015] The present invention provides an imaging process comprising the steps of: (i) providing a laser addressable thermal transfer imaging element comprising a substrate having a first side and a second side, the first side having deposited thereon a transferable color layer, and the second side having a microstructured surface, wherein the microstructured surface has a gradual transition of refractive index from air to substrate and a reflectivity of less than or equal to 4%; (ii) placing in contact with the transferable color layer of the thermal transfer imaging element a receptor; (iii) exposing the thermal transfer imaging element with a coherent radiation source in an imagewise pattern, wherein the coherent radiation is directed onto the microstructured surface of the thermal imaging element; (iv) transferring a portion of the transferable color layer representing the imagewise pattern onto the receptor, wherein the transferred portion has no visual optical interference pattern within the imagewise pattern. The laser addressable thermal transfer imaging element may optionally include, in order, a light-to heat conversion layer and an optional interlayer interposed between the substrate and the transferable color layer. The transfer imaging element may also include a transparent adhesive layer deposited upon the transferable color layer.

[0016] In a preferred embodiment, the transfer imaging element includes a microstructured surface comprising a plurality of randomly positioned discrete protuberances having varying heights and shapes, or a boehmited aluminum surface, or a microporous hydrophilic silicated surface comprising a colloidal silica optionally crosslinked with a coupling agent.

Detailed Description

[0017] Laser induces thermal imaging elements, to date, suffer reduced image quality due to scatter or reflection of the coherent radiation at the air/substrate and substrate/coating layer interfaces. The reflection of the coherent radiation compounded with minute variations in the layer thickness of the thermal transfer element form visual non-uniformities in the image. The minute variations allow the coherent imaging radiation to form optical interference patterns which alter the effective imaging intensity (higher or lower) of the radiation in a random pattern, thus imparting a corresponding visual interference pattern in the final image. This visual interference pattern is not to be confused with a moiré pattern, which is an optical illusion caused by misalignment or incorrect screen angles when two or more screen patterns are placed over one another.

[0018] Even though the interference pattern may be visually detected with the naked eye, the corresponding measurements with a densitometer are typically within the error of the measuring instrument. Therefore, the acceptable level of visual interference patterns is evaluated with the naked eye. This is a very subjective method and varies depending upon the observer and the image being observed. To address this ambiguity, the visual interference patterns were evaluated by generating a repetitive parallel line image having a resolution of 80 or greater dots-per-cm (dots/cm), i.e. 200 or greater dots-per-inch (dpi)). The imaged films were then observed with the naked eye at a distance of 30 centimeters

(cm). Therefore, in the context of the present invention the term "no visual interference pattern" means no detectable visual interference pattern within a parallel line image pattern having a resolution of ≥ 80 dots/cm (200 dpi) at a distance of 30 cm using the naked eye as the observer.

[0019] The present invention utilizes a microstructured surface on the laser addressed surface of a thermal imaging element to reduce the formation of optical interference patterns. The thermal imaging element comprises a substrate having coated thereon a thermal transfer of ablative system opposite to the laser addressed microstructured surface. Suitable substrates include; plastic sheets and films, such as, polyethylene terephthalate, fluorene polyester polymers, polyethylene, polypropylene, acrylics, polyvinyl chloride and copolymers thereof, and hydrolyzed and non-hydrolyzed cellulose acetate. The substrate needs to be sufficiently transparent to the imaging radiation emitted by the laser or laser diode to effect thermal transfer of the corresponding image to a receptor sheet.

[0020] The microstructured surface may be composed of a plurality of randomly positioned discrete protuberances of varying heights and shapes. The protuberances are generally columnar (e.g., spire-shaped) with a height ranging from 10 to 1500 nanometers (nm) and are separated from adjacent protuberances at a distance ranging from 3 to 500 nm (as measured from the tips of the protuberances). Microstructured surfaces of this type may be prepared by the methods described in U.S. Patent Nos. 4,340,276 or 4,396,643; the method disclosed in U.S. Patent No. 4,340,276 being preferred.

[0021] In accordance with U.S. Patent No. 4,340,276, the microstructured surface can be formed by first selecting a substrate having a predetermined rate of sputter etching under a given set of sputtering conditions. A material having a lower rate of sputter etching under the same set of conditions (e.g., a refractory metal such as chromium) is then applied to the substrate in an average thickness in the range of 0.1 to 10 nm, thereby forming a composite surface on which portions of the underlying substrate are exposed between discontinuous micro-islands of the lower sputter rate material. Finally, the composite surface is sputter etched to preferentially etch the exposed portions of the higher sputtering rate substrate, while the discontinuous micro-islands are etched at a lower rate, resulting in a topography of randomly positioned discrete protuberances of varying heights and shapes.

[0022] Alternatively the microstructured surface may be a boehmited aluminum surface. The boehmited surface may be generated using methods described in U.S. Patent Nos. 4,190,321 and 4,252,843. A thin-film of aluminum is first deposited onto an appropriate substrate to a thickness of between 30 to 50 nm. A typical method of deposition of aluminum is vapor deposition. The deposited aluminum surface is then converted to an aluminum oxide or hydroxide by exposing the film to water for an appropriate duration and at a temperature until the metal layer becomes transparent and exhibits the requisite decrease in reflectivity. The conversion may be accomplished by exposing the aluminum surface to saturated steam or by immersing the film in aqueous oxidizing solutions. The treatment time ranges from approximately 0.5 to 20 minutes depending upon the process temperature.

[0023] The microstructured surface may also consist of finely dispersed silica particles which may be crosslinked by a coupling agent and adhered to the polymeric substrate. The microstructured silicated surface is prepared by coating an aqueous solution comprising a colloidal silica sol and an optional ambifunctional silane coupling agent on the polymeric surface of the substrate of a the thermal transfer element. The colloidal silicas are different from silica powders in that they are discrete, non-agglomerated and uniformly dispersed in a liquid medium. The surface of the colloidal particle comprises pay ionized silanol groups which are stabilized by a counter ion. Suitable silica sols non-exclusively include; sodium, potassium and ammonium stabilized colloidal silica dispersions, such as those available under the trade designations Nalco 2326 and 2327 which are commercially available from Nalco Chemical, Chicago, IL. The preferred mean particle size is from 2 to 100 nm, and more preferably from 4 to 50 nm.

[0024] Suitable coupling agent; are ambifunctional silanes which have reactive silane groups on one end of the molecule and another different functional group capable of chemical reacting with or bonding to the substrate or primer on the substrate. The coupling agent; are materials well known in the art, as represented by EPO Application 0 301 827 A2. Those silanes are ambifunctional silane coupling agents represented by the formula:

$$(Q)_n\text{---}R\text{---}Si(OR^1)_3$$
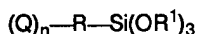
wherein:

R^1 is an alkyl or aryl group,
R is an organic group with (n+1) external bonds or valences, where n is 0, 1 or 2, and
Q is a moiety reactive with the substrate or primer on the substrate.

[0025] Preferably R^1 is alkyl of 1 to 10 carbons atoms and most preferably 1 to 4 carbon atoms. R is preferably an aliphatic or aromatic bridging group such as alkylene, arylene, alkarylene, or aralkylene which may be interrupted with ether linkages (oxygen or thioethers), nitrogen linkages, or other relatively inert moieties. More preferably R is alkylene of 1 to 12 carbon atoms, preferably 2 to 8 carbon atoms, with n equal to 1. Q is preferably epoxy, or amino, primary or

secondary, more preferably primary amino.

[0026] Where previously indicated that the second functional group may be present as a multiple number of such groups it is meant that the moiety $(Q)_n$—R— may include moieties such as:

$$NH_2—(CH_2)_2—NH(CH_2)_2—NH—(CH_2)_3—$$

$$NH_2—(CH_2)_3—$$

$$(NH_2)_2—CH—CH_2—$$

$$(NH_2—CH_2)_2—CH—$$
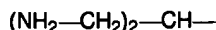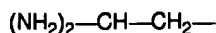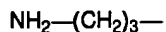
[0027] The ratio of the colloidal silica to the silane coupler in the coating solution is generally from 15:1 to 4:1 by weighs depending on which silica and silane are used. For example, when Nalco 2326 colloidal silica with a mean particle size of 5 nm and pH of 9.0 is to be crosslinked with 3-aminopropyl triethoxysilane, their useful ratio is between 12.5:1 to 5:1 by weight. The coating solutions may combine with other materials such as coating aids, surfactants, binders, etc., in amounts sufficient to improve coating quality and not adversely effect the desired microporosity. These additives can be added in amounts in the range of 0.01 to 5.0% by weight of the colloidal silica. The resulting solutions are coated by methods known in the art and dried at 100 - 120°C to yield a dry coating weight of 0.1 to 2 g/m^2 with a thickness between 0.08 to 0.25 µm.

[0028] The microstructured surfaces described above maximize the transmittance of the laser light and minimize the reflection of the laser light by effectively providing a gradual transition of refractive index from air to substrate. The microstructured surface preferably has a reflectivity less than or equal to 4%. Examples of refractive gradient index profile models for a variety of microstructured films using computational methods are described in P.K Lee and M.K Debe, *Photograhic Science and Engineering* "Measurement and Modeling of the Reflectance-Reducing Properties of Gradient Index Microstructured Surfaces", **24**, 211 (1980).

[0029] "thermally melt stick materials" include thermal mass transfer materials which when thermally addressed stick to a receptor surface with greater strength than they adhere to the donor surface and physically transfer when the surfaces are separated. The above two processes may be used equivalently to other methods within the concept of laser induced mass transfer for generating colors.

[0030] "Transparentize" or "transparentization" refers to a process in which a substantial increase in the light transmissivity of the medium is observed (e.g., through vaporization, oxidation, ablation, melt and roll back, etc. of the black coating layer).

[0031] In the practice of the invention, a suitable thermal transfer element consists of a transferable color layer comprising a coating of a dye or pigment (with or without a binder) on a substrate. A coherent radiation source, such as a laser or laser diode, is used to expose and heat the colored material in an imagewise pattern thus transferring the transferable color layer to the receptor sheet to form a colored image. It is often desirable in such constructions to assist in the absorption intensity of the imaging radiation since the dye or pigment (and the substrate) may not necessarily be highly absorptive of the imaging radiation. An imaging radiation absorbent material may be included within the dye/pigment layer (e.g., where an infrared emitting imaging radiation source is used, an infrared (IR) absorbing dye with little or no visible absorbance may be used). A separate imaging radiation absorbing layer may also be used, normally adjacent to the color containing donor layer. The colors of the donor layer may be selected as needed by the user from amongst the many available colors, such as cyan, yellow, magenta, red, blue, green, white and other colors and tones of the spectrum are contemplated.

[0032] A typical thermal melt stick transfer element comprises a substrate and deposited thereon, in order; a light-to-heat-conversion layer (LTHC), an optional interlayer, a colorant layer, and an optional adhesive layer. The substrate is preferably a polyester film. However, any film that has sufficient transparency at the imaging wavelength and sufficient mechanical stability can be used.

[0033] The LTHC layer can be any infrared absorber which converts the infrared radiation into heat. Preferably, the LTHC layer has an optical density between 0.2 and 3.0. Suitable examples include: carbon black, bone black, iron oxide, copper/chrome complex black azo pigment (e.g. pyrazolone yellow, dianisidine red, and nickel azo yellow, black aluminum, and phthalocyanine pigments). Alternatively, the radiation absorber may be a dye as described, for example in Matsuoka, M., Absorption Spectra of Dyes for Diode Lasers, Bunshin Publishing Co., Tokyo, (1990). A preferred LTHC layer is a metal/metal oxide layer (e.g. black aluminum), such as those described in U.S. Patent No. 4,430,366.

[0034] In accordance with U.S. Patent No. 4,430,366, a black aluminum layer can be applied to the substrate in conventional vapor deposition environments into which there is the controlled release of one or more of the following reactive materials: oxygen, water vapor, sulphur vapor, or hydrogen sulfide. Controlled conversion of the metal to metal oxides or metal sulfides is effected by the controlled introduction of these materials into a metal vapor stream of a con-

ventional vapor deposition apparatus during the vapor deposition of metals onto the substrate.

[0035] Substantially any metal capable of forming an oxide or sulfide can be used in the practice of this invention for the black metal layer. In particular aluminum, tin, chromium, nickel, titanium, cobalt, zinc, iron, lead, manganese, copper and mixtures thereof can be used. Not all of these metals when converted to metal oxides according to this process will
5 form materials having all of the specifically desirable properties (e.g., optical density, light transmissivity, etc.). However, all of these metal oxide containing layers formed according to the practice of the present invention will be useful and contain many of the benefits of the present process including bondability to polymeric materials. The metal vapors in the chamber may be supplied by any of the various known techniques suitable for the particular metals, e.g., electron beam vaporization, resistance heaters, etc. Reference is made to Holland, L., Vacuum Deposition of Thin Films, Chap-
10 man and Hall, London, England (1970) with regard to the many available means of providing metal vapors and vapor coating techniques, in general.

[0036] Metal oxide or metal sulfide containing layers, exemplary of the black metal layers, may be deposited as thin as layers of molecular dimensions up through dimensions in micrometers. The composition of the layer throughout its thickness may be readily controlled as herein described. Preferably the metal/metal oxide or sulfide layer will be
15 between 5 and 50 nm in its imaging utilities, but may contribute bonding properties when 1.5 nm, 2.5 nm or smaller and structural properties when 5000 nm or higher.

[0037] The conversion to graded metal oxide or metal sulfide is effected by the introduction of oxygen, sulfur, water vapor or hydrogen sulfide at points along the metal vapor stream. By introducing these gases or vapors at specific points along the vapor stream in the vapor deposition chamber, a coating of a continuous or graded composition
20 (throughout either thickness of the layer) may be obtained. By selectively maintaining a gradation of the concentration of these reactive gases or vapors across the length of the vapor deposition chamber through which the substrate to be coated is being moved, an incremental gradation of the composition of the coating layer (throughout its thickness) is obtained because of the different compositions (i.e., different ratios of oxides or sulfides to metals) being deposited in different regions of the vapor deposition chamber. One can in fact deposit a layer comprising 100% metal at one surface
25 (the top or bottom of the coating layer) and 100% metal oxide or sulfide at the other surface. This kind of construction is a particularly desirable one because it provides a strong coherent coating layer with excellent adhesion to the substrate.

[0038] A substrate which is to be coated continuously moves along the length of the chamber from an inlet area of the vapor deposition chamber to an outlet area. Metal vapor is deposited over a substantial length of the chamber, and
30 the proportion of metal oxide or sulfide being co-deposited with the metal at any point along the length of the chamber (or deposited as 100% oxide or sulfide) depends upon the amount of reactive gas or vapor which has entered that portion of the metal vapor stream which is being deposited at that point along the length of the chamber. Assuming, for purposes of illustration, that an equal number of metal atoms (as metal or oxides or sulfides) are being deposited at any time at any point along the length of the chamber, gradation in the deposited coating is expected by varying the amount
35 of oxygen or sulfur containing reactive gas or vapor which contacts the metal vapor at various points or areas along the length of the chamber. By having a gradation of increasing amounts of reactive gas along the length of the chamber, one gets a corresponding gradation in the increased proportions of oxide or sulfide deposited. Deposition of metal vapor is seldom as uniform as that assumed, but in actual practice it is no more difficult according to the procedures of the present invention to locally vary the amount of oxygen, water, sulfur or hydrogen sulfide introduced into different
40 regions of said metal vapor along the length of the surface of the substrate to be coated as the substrate is moved so as to coat the surface with a layer having varying ratios of metal/(metal oxide or sulfide) through its thickness. It is desirable that the reactive gas or vapor enter the stream itself and not just diffuse into the stream. The latter tends to cause a less controllable distribution of oxides within the stream. By injecting or focusing the entrance of the reactive gas or vapor into the stream itself, a more consistent mixing in that part of the stream is effected.

45 [0039] Transitional characteristics bear an important relationship to some of the properties of the black metal products. The coating has dispersed phases of materials therein, one the metal and the other the metal oxide or sulfide. The latter materials are often transparent or translucent, while the former are opaque. By controlling the amount of particulate metal which remains dispersed in the transparent oxide or sulfide phase, the optical properties of the coating can be dramatically varied. For example, U.S. Patent No. 4,387,156 describes translucent coatings of yellowish, tan, and
50 gray tones and substantially opaque black film from a single metal by varying the percentage of conversion of the metal to oxide during deposition of the coating layer.

[0040] Adjacent to the LTHC layer is an optional interlayer which is particularly useful in thermally melt stick materials to prevent the LTHC layer from contaminating the colorant layer during the image transfer process. A typical interlayer comprises a cross-linked polymer, such as a photopolymerizable multiacrylate oligomer and/or monomer combined
55 with a photoinitiator system, or organic polymers having a glass transition temperature greater than 150°C, such as Radel™ A-100 (acrylic emulsion available from Amoco Performance Products, Chicago, IL).

[0041] Adjacent to the optional interlayer is a color layer which comprises at least one organic or inorganic colorant or pigment and optionally an organic polymer or binder. The color layer may also contain a variety of additives including

but not limited to dyes, plasticizers, UV-stabilizers, film forming additives, and adhesives. When a dye is used as an additive, it is generally preferable that the dye absorbs light of the same frequency as the imaging light source.

[0042] In a preferred embodiment, the color layer includes a pigment, surfactant, binder, and possibly other additives. Any pigment may be used, but preferred are those listed as having good color permanency and transparency in the NPIRI Raw Materials Data Handbook, Volume 4 (Pigments). Either non-aqueous or aqueous dispersions of pigment in binder may be used. In the non-aqueous case, solvent based pigment dispersions may be used along with an appropriate solvent based binder (i.e. Elvacite™ acrylic resins available from E.I. Du Pont de Nemours). However, it is often preferred to use an aqueous dispersion of pigment in binder. In this case, the most preferred pigments are in the form of binderless aqueous dispersions (i.e., Aquis II™ supplied by Heucotech) and the most preferred binders are those specifically designed for pigment wetting (i.e. Neocryl BT™ acrylic resins from Zeneca Resins). The use of appropriate binders promotes the formation of sharp, well defined lines during transfer. When the colorant transfer is induced by a high powered light source (i.e., xenon flash lamp), it is usually necessary to include as binder an energetic or gas producing polymer such as disclosed in U.S. Pat. Nos. 5,308,737 and 5,278,023.

[0043] The pigment/binder ratio is typically 1:1 but may range from 0.25:1 to 4:1. A wire wound bar may be used to coat the colorant layer. Typically, a #4 bar is used to coat the dispersion which contains approximately 10 wt. % solids to give a dry coating thickness of about 1 μm. Other combinations of dispersion % solids and wire wound bar number are used to achieve different coating thickness. In general, a dry coating thickness of 0.1 to 10 μm is desired.

[0044] An optional adhesive layer may be provided on the outermost layer of the donor or receptor to assist in the transfer process The adhesive serves to promote complete transfer of colorant during the separation of the donor from the receptor after imaging. Preferred adhesives are colorless, transparent materials with a slight tack or no tack at room temperature, such as, (meth)acrylates, vinyl (meth)acrylates, vinyl acetates, etc.

[0045] The transfer process may be performed by fairly simple steps, which is one of the major advantages of the present invention. A laser or other focused radiation source is used to heat the thermal mass transfer layer either directly or by means of the LTHC layer in an imagewise pattern in order to transfer the thermal mass transfer material to the receptor sheet.

[0046] Suitable receptors a well known to those skilled in the art. Non-limiting examples of receptors which can be utilized in the present invention include anodized aluminum and other metals; transparent polyester films, glass, and a variety of different types of paper (e.g. , filled or unfilled, calendered, coated, etc.).

[0047] Other suitable imaging elements for use in the present invention include ablative systems. An example of a suitable direct ablating element consists of a LTHC layer with a substantial white light transmission optical density (TOD) of at least 0.2 coated onto a substrate. Other suitable constructions are described, for example, in EP-A-0 562 952 which discloses ablative imaging elements comprising a substrate coated with an energy sensitive layer comprising a glycidyl azide polymer in combination with a radiation absorber; and U.S. Patent No. 5,308,737 which discloses the use of black metal layers on polymeric substrates with gas-producing polymer layers which generate relatively high volumes of gas when irradiated. The black metal (e.g., aluminum) absorbs the radiation efficiently and converts it to heat for the gas-generating materials.

[0048] Like the transfer process, the ablative process may be performed by fairly simple steps as well. A laser or other focused radiation source is used to heat the ablative layer directly or by means of an underlying LTHC layer in an imagewise pattern in order to ablate away the non-imaged areas of the film. The non-imaged areas become transparentized thus leaving a visible image in the non-light struck areas.

[0049] A variety of light-emitting sources can be utilized in the present invention including infrared, visible, and ultraviolet lasers. The preferred lasers for use in this invention include high power (greater than 100 milliWatts) single mode laser diodes, fiber-coupled laser diodes, and diode-pumped solid state lasers (e.g., Nd:YAG and Nd:YLG). The laser exposure should raise the temperature of the thermal transfer medium above 150°C and most preferably above 200°C. Laser exposure dwell times should be from about 0.1 to 5.0 microseconds and laser fluences should be from about 0.01 to about 1 Joule/cm^2.

[0050] The following non-limiting examples further illustrate the present invention.

Examples

[0051] The following examples illustrate the comparative effect of adding a coating having a graded index refraction onto the laser addressed surface of a thermal transfer imaging element. The Examples below were prepared using the following black coating solution for the LTHC layer:

Black coating solution:

Furnace carbon black dispersion (37% by weight in water; 50-9410 available from RBH Dispersions, Inc.)	13.5 g
Ethanol	86.5 g
FC430 (trade designation for a fluorocarbon surfactant available from 3M, St. Paul, MN)	0.1 g

[0053] The sputter etched microstructured polyester film used in the Examples was prepared as follows;

Sputter etched microstructured polyester film:

[0054] The microstructured polyester film was produced in accordance with US. Patent No. 4,340,276 by sputter coating a 0.08 mm (3 mil) polyester with Cr, and etching with oxygen plasma. The features of the resulting materials were tapering columns irregularly distributed on the film with radii of 5-50 nm and heights of about 100-200 nm. The columns were spaced from one another by 75-300 nm. The resultant sputter etched film had a reflectivity of 4% at the sputter etched polyester/air interface.

[0055] The imaging elements for each Example were imaged using a sensitometer equipped with a Nd:YLG laser. A rotating mirror was used to sweep the imaging beam across a lens which focused the beam to a 26 micrometer spot ($1/e^2$). The power on the film plane was 3.2 Watts and the beam scan speed was 6400 centimeters /second. In the following examples, the direct ablating element was placed in vacuum contact with a plain paper substrate with the LTHC layer in direct contact with the paper. The laser beam was directed onto the light-absorbing LTHC coating through the polyester substrate. Line segments were ablated from the imaging element. The outermost fringes of the transferred or ablated segment represented the onset of the imaging process. Therefore, the linewidth at a given scan speed corresponded to the sensitivity of the element. The presence of an interference pattern in the line image was evaluated visually with the naked eye. Table 1 summarizes the imaging results observed for Examples 1-11.

Example 1

[0056] The black coating solution was coated onto a 0.10 mm (4 mil) polyester substrate using a #4 wire wound bar. The coating was then dried at 80°C for 1 minute. The carbon black/polyester interface had a reflectivity of 4%.

Example 2

[0057] An anti-reflection coating, comprising a 2.0% by weight solution of 10 parts Nalco 2326 colloidal silica (ammonium stabilized colloidal silica with a mean particle see of 5 nm, available from Nalco Chemical, Chicago, IL) and 1 part Triton™ X-100 (octylphenoxy ethanol, available from Rohm & Haas, Philadelphia, PA) in water, was coated onto a 0.10 mm (4 mil) polyester substrate using a #8 wire wound bar. The coating was dried at 80°C for 1 minute resulting in an approximate dry coating thickness of 0.03 μm. The black coating solution was then coated onto the polyester surface opposite the anti-reflection coating using a #4 wire wound bar. The coating was then dried at 80°C for 1 minute.

Example 3

[0058] An anti-reflection coating, comprising a 2.0% by weight solution of 10 parts Nalco 2326 colloidal silica (ammonium stabilized colloidal silica with a mean particle size of 5 nm, available from Nalco Chemical, Chicago, IL) and 1 part Triton™ X-100 (octylphenoxy ethanol, available from Rohm & Haas, Philadelphia, PA) in water, was coated onto both sides of a 0.10 mm (4 mil) polyester substrate at a dry coating thickness of 0.03 μm. The coatings were dried at 80°C for 1 minute. The black coating solution was then coated onto one of the anti-reflection coating layers using a #4 wire wound bar. The coating was then dried at 80°C for 1 minute.

Example 4

[0059] The black coating solution was coated onto the non-microstructured side of 0.10 mm (4 mil) sputter etched polyester substrate using a #4 wire wound bar. The coating was then dried at 80°C for 1 minute.

Example 5

[0060] The black coating solution was coated onto the microstructured side of the 0.10 mm (4 mil) sputter etched polyester substrate using a #4 wire wound bar, The coating was then dried at 80°C for 1 minute.

Example 6

[0061] An aluminum vapor coat was applied to a 0.10 mm (4 mil) polyester substrate at an approximate thickness of 8.1 nm. The black coating solution was coated onto the aluminium layer using a #4 wire wound bar. The coating was then dried at 80°C for 1 minute.

Example 7

[0062] An aluminium vapor coat was applied to a 0.10 mm (4 mil) polyester substrate at an approximate thickness of 8.1 nm. An anti-reflection coating, comprising a 2.0% by weight solution of 10 parts Nalco 2326 colloidal silica (ammonium stabilized colloidal silica with a mean particle size of 5 nm, available from Nalco Chemical, Chicago, IL) and 1 part Triton™ X-100 (octylphenoxy ethanoL available from Rohm & Haas, Philadelphia, PA) in water, was coated onto the polyester surface opposite the aluminum vapor coat using a #8 wire wound bar. The coating was dried at 80°C for 1 minute resulting in an approximate dry coating thickness of 0.03 μm. The black coating solution was then coated onto the aluminum layer using #4 wire wound bar. The coating was then dried at 80°C for 1 minute.

Example 8

[0063] A sublimable dye coating solution comprising a 0.25% by weight solution of 4 parts DY11 (C.I. Disperse Yellow 11, available from L.B. Holliday & Co. Ltd., London, England) to 5 parts AC330 (trade designation for a polyethylene aqueous emulsion available from Chemcor Chemical Corporation, New Salem, NY) was coated onto a 0.10 mm (4 mil) polyester substrate. The coating was dried at 80°C for 1 minute. An aluminum vapor coat was then applied over the sublimable dye layer at an approximate thickness of 8.1 nm. The black layer was then coated over the surface of the aluminum layer using a #4 wire wound bar. The black coating was dried at 80°C for 1 minute.

Example 9

[0064] The imaging element described in Example 8 was coated with an anti-reflection coating comprising a 20% by wet solution of 10 parts Nalco 2326 colloidal silica (ammonium stabilized colloidal silica with a mean particle size of 5 nm. available from Nalco Chemical, Chicago, IL) and 1 part Triton™ X-100 (octylphenoxy ethanol, available from Rohm & Haas, Philadelphia, PA) in water, onto the non-coated surface of the polyester substrate using a #8 wire wound bar. The coating was dried at 80°C for 1 minute resulting in an approximate dry coating thickness of 0.03 μm.

Example 10

[0065] A 0.1% by weight solution of Polyfoam FC722 (trade designation for a fluorocarbon polymer available from 3M, St. Paul, MN) was coated onto a 0.10 mm (4 mil) polyester substrate using a #3 wire wound bar. An aluminum vapor coat was then applied over the polyfoam layer at an approximate thickness of 8.1 nm. The black layer was then coated over the surface of the aluminum layer using a #4 wire wound bar. The black coating was dried at 80°C for 1 minute.

Example 11

[0066] The imaging element described in Example 10 was coated with an anti-reflection coating, comprising a 2.0% by weight solution of 10 parts Nalco 2326 colloidal silica (ammonium stabilized colloidal silica with a mean particle size of 5 nm, available from Nalco Chemical, Chicago, IL) and 1 part Triton™ X-100 (octylphenoxy ethanol, available from Rohm & Haas, Philadelphia, PA) in water, onto the non-coated surface of the polyester substrate using a #8 wire wound bar. The coating was dried at 80°C for 1 minute resulting in an approximate dry coating thickness of 0.03 μm.

Example 13

[0073] Example 13A1 was made by sputter coating black aluminum onto an unprimed 0.10 mm (4 mil) polyester film. The surface reflectivity of Example 13A1 was measured at 1.06 μm which represents the wavelength of the Nd:YAG laser. The aluminum surface had a reflectivity of 56% and the polyester surface a reflectivity of 39%.

[0074] A comparative Example 13B1 was prepared by coating an interlayer and color layer onto Example 13A1. The interlayer consisting of a 5% by weight solution of Radel™ A-100 (acrylic aqueous emulsion available from Amoco Performance Products, Chicago, IL) was coated onto the aluminum solace using a #6 wire wound bar. A color layer consisting of a 15% total solids dispersion of 59% by weight Pigment Green 7 (available from Allegheny Chemical Corp., Ridgway, PA), 39.6% by weight of Elvacite™ 2776 acrylic resin (available from E I. Du Pont Nemours & Co., Inc., Wilmington, DE) and 1% by weight Triton™ X-100 (available from Rohm & Haas, Philadelphia, PA) was coated onto the interlayer surface using a #3 wire wound bar.

[0075] Example 13B1 was placed on the top of a clean glass plate with the color layer in intimate contact with the glass surface using a vacuum frame. The Example was imaged by focusing a 7 Watt Nd:YAG laser through a flat-field lens to a spot size of 100 μm and scanning at a scan rate of 8 meters/second. The laser was directed onto the aluminum layer through the polyester substrate. The laser caused the exposed areas to heat up to an elevated temperature thus enabling the color layer to transfer to the glass plate. The high reflectivity of the aluminum/polyester interface at the laser wavelength caused severe interference patterns in the transferred parallel line images.

[0076] Example 13B2 was prepared by coating the uncoated polyester surface of Example 13B1 with an anti-reflection coating consisting of a 4.5% by weight solution of 10 parts Nalco 2327 colloidal silicia (available from Nalco Chemical, Chicago, IL) and 0.5 parts Triton™ X-100 (available from Rohm & Haas, Philadelphia, PA) in a 1:1 mixture of ethanol and water. The coating was applied to the polyester surface using a #4 wire wound bar and then dried at 80°C for 1 minute.

[0077] Example 13B2 was imaged in the same manner as Example 13B1. The transferred color image showed no visual interference patterns. The parallel line images had uniform widths with good resolution.

[0078] Even though the microstructured surfaces produced through sputter-etching of the polyester film do not reduce the surface reflectivity as much as colloidal silica coatings at the appropriate thicknesses, they are still effective in reducing or even eliminating the interference patterns in laser induced thermal imaging systems when the LTHC/polyester interface has a low reflectivity. These observations are particularly illustrated in Examples 1-11 where the LTHC layers consist of low reflective black carbon coatings.

Claims

1. An imaging process comprising the steps of:

    (i) providing a laser addressable thermal transfer imaging element comprising a substrate having a first side and a second side;
    (ii) placing in contact with said first side of said thermal transfer imaging element a receptor;
    (iii) exposing said thermal transfer imaging element with a coherent radiation source in an imagewise pattern, wherein said coherent radiation is directed onto the second side of said thermal imaging element; and
    (iv) transferring a portion of said first side representing said imagewise pattern onto said receptor, wherein said portion has no visual optical interference pattern within said imagewise pattern;
    characterized in that said first side of said thermal transfer imaging element has deposited thereon a transferable color layer, and said second side of said thermal transfer imaging element has a microstructured surface, wherein said microstructured surface has a gradual transition of retractive index from air to substrate and a reflectivity of less than or equal to 4%.

2. The imaging process of Claim 1 wherein said laser addressable thermal transfer element further comprises a transparent adhesive layer deposited upon said transferable color layer.

3. The imaging process of Claim 1 wherein said microstructured surface comprises a plurality of randomly positioned discrete protuberances having varying heights and shapes.

4. The imaging process of Claim 1 wherein said microstructured surface is a boehmited aluminum surface.

5. The imaging process of Claim 1 wherein said microstructured surface is a microporous hydrophilic silicated surface comprising a colloidal silica.

6. The imaging process of Claim 5 wherein said silicated surface is crosslinked with a coupling agent.

Patentansprüche

1. Abbildungsverfahren mit den folgenden Schritten:

(i) Bereitstellen eines laseradressierbaren Thermotransfer-Abbildungselements mit einem Substrat, das eine erste Seite und eine Zweite Seite hat;
(ii) In-Berührung-bringen eines Empfängers mit der ersten Seite des Thermotransfer-Abbildungselements;
(iii) Belichten des Thermotransfer-Abbildungselements mit einer kohärenten Strahlungsquelle in einem bildweisen Muster, wobei die kohärente Strahlung auf die zweite Seite des Thermoabbildungselements gerichtet wird; und
(iv) Transferieren eines Abschnitts der ersten Seite als Darstellung des bildweisen Musters auf den Empfänger, wobei der Abschnitt kein sichtbares optisches Interferenzmuster innerhalb des bildweisen Musters hat;
dadurch gekennzeichnet, daß auf die erste Seite des Thermotransfer-Abbildungselements eine transferierbare Farbschicht abgeschieden ist und die zweite Seite des Thermotransfer-Abbildungselements eine mikrostrukturierte Oberfläche hat, wobei die mikrostrukturierte Oberfläche einen graduellen Brechzahlübergang von Luft zum Substrat und ein Reflexionsvermögen von höchstens 4 % hat.

2. Abbildungsverfahren nach Anspruch 1, wobei das laseradressierbare Thermotransferelement ferner eine transparente Klebstoffschicht aufweist, die auf die transferierbare Farbschicht abgeschieden ist.

3. Abbildungsverfahren nach Anspruch 1, wobei die mikrostrukturierte Oberfläche mehrere zufällig positionierte diskrete Ausstülpungen mit variierenden Höhen und Formen aufweist.

4. Abbildungsverfahren nach Anspruch 1, wobei die mikrostrukturierte Oberfläche eine mit Boehmit behandelte Aluminiumoberfläche ist.

5. Abbildungsverfahren nach Anspruch 1, wobei die mikrostrukturierte Oberfläche eine mikroporöse hydrophile silicierte Oberfläche mit einem kolloidalen Siliciumoxid ist.

6. Abbildungsverfahren nach Anspruch 5, wobei die silicierte Oberfläche mit einem Haftmittel vernetzt ist.

Revendications

1. Un processus d'imagerie qui comprend les étapes consistant à

(i) agencer un élément d'imagerie par transfert thermique adressable par laser qui comprend un substrat présentant un premier côté et un deuxième côté;
(ii) placer un récepteur au contact dudit premier côté dudit élément d'imagerie par transfert thermique;
(iii) exposer ledit élément d'imagerie par transfert thermique au moyen d'une source de rayonnement cohérent selon une configuration de type image, le rayonnement cohérent étant dirigé sur le deuxième côté dudit élément d'imagerie thermique; et
(iv) transférer sur ledit récepteur une partie dudit premier côté qui représente ladite configuration de type image, ladite partie ne comportant aucune interférence optique visuelle à l'intérieur de ladite configuration de type image;
caractérisé en ce qu'une couche colorée transférable est déposée sur ledit premier côté dudit élément d<imagerie par transfert thermique et ledit deuxième côté dudit élément d'imagerie par transfert thermique comporte une surface à microstructure, ladite surface à microstructure présentant une transition progressive d'indice de réfraction de l'air au substrat et une réflectivité inférieure ou égale à 4 %.

2. Le processus d'imagerie selon la revendication 1 dans lequel ledit élément d'imagerie par transfert thermique comprend en outre une couche adhésive transparente déposée sur ladite couche colorée transférable.

3. Le processus d'imagerie selon la revendication 1 dans lequel ladite surface à microstructure comprend une série de protubérances discrètes positionnées de façon aléatoire, à hauteurs et configurations variées.

4. Le processus d'imagerie selon la revendication 1 dans lequel ladite surface à microstructure est une surface d'alu-

minium convertie en boehmite.

5. Le processus d'imagerie selon la revendication 1 dans lequel ladite surface à microstructure est une surface silicatée hydrophile microporeuse comprenant de la silice colloïdale.

6. Le processus d'imagerie selon la revendication 5 dans lequel ladite surface silicatée est réticulée au moyen d'un agent de couplage.

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